

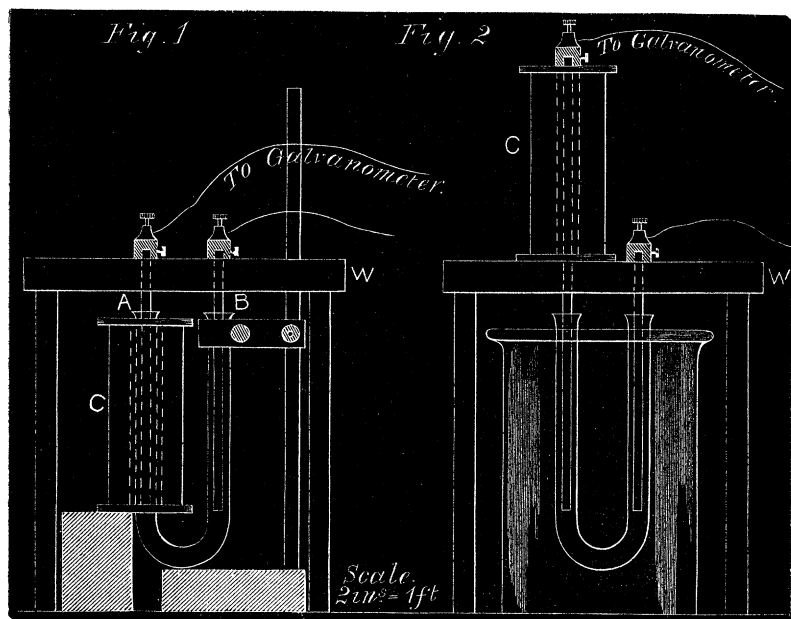
killed and pithed immediately after taken from the net, may pass into rigor in 30 minutes and be again quite limp 6 hours after death. Sometimes, however, the rigor may not set in for 2 hours after the fish are landed, and it may continue for 17 hours, the difference doubtless resulting partly from the difference in the time the fish were in the trawl net, and partly from the energy expended in attempting to escape, or in endeavouring to maintain the respiratory movements under somewhat difficult circumstances. It may therefore be affirmed that though the rigor may persist as long or nearly as long in some trawled fish as in fish caught with a line, in most cases the rigor disappears sooner from trawled than from line-caught fish; in other words, putrefaction sets in sooner as a rule in fish taken by the trawl than in fish taken by the line, granting, of course, that the line fish are pithed and gutted as soon as they leave the water.

I have, in conclusion, to express my gratitude to Professor Burdon Sanderson and Mr. Gotch for valuable assistance rendered with the experiments made in the Oxford Physiological Laboratory. I am also indebted to Professor Tait for kindly allowing Mr. Lindsay, of the Natural Philosophy Laboratory in the University of Edinburgh, to assist with the electrical experiments. I am further indebted to Mr. Clarkson, B.Sc., of the Natural History Department, Edinburgh, and Mr. W. L. Calderwood and Mr. Jamieson, Members of the Staff of the Fishery Board for Scotland.

XXVI. "Electrochemical Effects on Magnetising Iron." By THOMAS ANDREWS, F.R.S.E., F.C.S. Communicated by Professor G. G. STOKES, P.R.S. Received June 2, 1887.

Having for many years past been engaged in researches relating to the various aspects of the corrosion and oxidation of metals, nearly two years ago it occurred to me to investigate the probable effect of magnetisation on the relative electrochemical position of a pair of bright iron bars, one magnetised by a coil, the other unmagnetised, when thus simultaneously exposed in circuit, in a suitable apparatus, to the action of various powerful oxidising agents and saline solutions. I accordingly specially prepared numerous long polished rods of soft wrought scrap iron 0.261 inch diameter, for use in the investigation. I was not able to commence the preliminary observations until towards the end of 1885, and, after much consideration and various trials then made, decided to adopt the following method of experimentation as perhaps calculated to yield the most delicate and accurate results; pressure of other work has, however, delayed the earlier completion of the work. The general

arrangement and methods of experimentation pursued are described below, and the apparatus is delineated on fig. 1 and fig. 2.



Two pieces were adjacently cut from a long finely polished iron rod, so that the pieces might as near as practicable be of identical chemical composition and molecular constitution. After being firmly placed and adjusted as to equal length, &c., in the wooden supporting frame W, they were immersed to an exactly equal depth in the solution contained in the U-tube, which latter was also rigidly supported by a stand. In the duplex experiments made with apparatus fig. 2, the U-tube was immersed in a large volume, four pints, of cold water to ensure equal temperature conditions during experimentation for the respective solutions in each limb, the cold water being maintained in steady circulation around the tubes. The rods were connected in circuit with a sensitive galvanometer, having a resistance of 521 ohms, and of known calibration, the galvanometer being under constant telescopic observation during the experiments, and the normal galvanic action between the two bars previously observed in every experiment. Considerable care was requisite to obtain this accurately, so as not practically to interfere with the subsequent results seemingly due to magnetic influences. A removable coil C, of stout silk-covered copper wire (No. 16 gauge) mounted on a large wooden bobbin 6 inches long enclosed the limb A of the U-tube, or when using apparatus fig. 2,

the coil surrounding the upper portion of the long bar requiring magnetisation. The coil used in the experiments with apparatus fig. 1 consisted of six depths or wraps of the insulated copper wire, each wrap having 81 turns, making in the whole a coil of 486 convolutions. The other coil employed in the experiments with apparatus fig. 2 was of similar construction, but had ten depths of insulated copper wire of the same thickness, constituting a coil with a total of about 750 convolutions.

A single cell bichromate battery, easily put in or out of operation, was attached to the coil, and the battery was recharged with the same strength of solution for each observation. After a suitable time had been allowed in each experiment for steady galvanic equilibrium to be established between the two iron rods, in the solution in the tubes, which took place at periods varying with the nature of the solution, the coil was put into operation. In the experiments with fig. 2 the end of the bar in the solution was the S seeking pole. It was most interesting to observe the result. The rod A thus magnetised in most of the solutions became the metal positive, the galvanometer indicating its steadily increasing electrochemical positive position compared with that of the unmagnetised bar B. Repeated careful experimentation appeared to indicate that the increased positivity of the rod A observed under these conditions was due to the increased action of the acid or saline solution on the iron rod which was under magnetic influence, owing to which it became surrounded by a slightly stronger saline solution than the other unmagnetised rod B, which was apparently less acted upon. In some cases in the more powerfully acid solutions, Table A, columns 4, 5, 7, 8, a kind of maximum point seemed to be generally reached, and after the more violent action of the acid had expended itself, a reduction of the E.M.F. between the rods was generally noticed as the solution in the B-tube gradually approached an equilibrium of composition compared with the solution in the A limb of the U-tube, and subsequently a reverse action in some cases was observed. The unmagnetised rod B appeared to be less rapidly acted upon than the one under magnetic influence. On magnetisation of the bar the above full effect on the galvanometer was not always of an instantaneous character, though a short time only appeared requisite for its development. The solutions employed are given in Table A, and the results therein recorded were derived from a series of constant observations, a comparison in some instances being afforded between the respective effects obtained by the two forms of apparatus employed.

It may be noticed that a fresh pair of the iron rods, cut adjacently from a long polished rod, were used for each experiment, and 123 pairs were used in course of this part of the investigation, the whole of the experiments being many times repeated to ensure

accuracy, the results recorded being the average of many observations. In some instances somewhat higher results were noticed.

It is almost impossible to obtain two pieces of iron (even when forming adjacent parts of one polished rod) which when in solution are devoid of some slight galvanic action between themselves; but the greatest care was exercised in the special preparation of the iron used, so that this variation might be reduced to a minimum.

To ensure success in the experiments it was found essential that the iron bars should possess an excellent polished surface, free from magnetic or other oxide or impurities; the solutions were also concentrated, and both discrimination and manipulative skill were requisite in obtaining the practical galvanic equilibrium of the bars at commencement. The time needed to ensure this seemed to vary considerably with different solutions according to circumstances. A sensitive galvanometer was also a requisite of success in these observations, and telescopic readings were necessary, as in some cases the effects were small.

It seems desirable here to add a few remarks on the possible influence of temperature on the reactions, and to state the means used in the endeavour to minimise errors from this source. In conducting the experiments, I should have preferred using greater battery power, but employed only one bichromate cell; the wire of the coil was also of considerable thickness to prevent undue heating from resistance. The centre of the wooden coil bobbin was also about

inch in thickness, so as to act as a central non-conductor. Moreover, an air space was allowed of  $\frac{1}{8}$  inch between the wooden centre of the coil and the enclosed limb of the U-tube. The other limb for the unmagnetised bar was enclosed by another coil, which, when not in use, acted as an external protective jacket. Notwithstanding these precautions, there was a slight increase of temperature in the interior of the coil C. Thermometers inserted in test solutions, one in each limb, gave an average difference of about  $1^{\circ}$  Fahrenheit at the end of an hour, this increase of temperature in the solution in the coil tube being, however, very gradual. It would be untenable to state that this difference of temperature, arising from the action of the coil, did not to some slight extent influence the results of the experiments with apparatus fig. 1; but the results obtained therewith could certainly not be regarded as due only to differences of temperature conditions between the two tubes. Most of the experiments with that apparatus afford within themselves evident proof to the contrary; thus, it will be seen, that the magnetised bar assumed a prominent positive position almost immediately after magnetisation, in the case of nitric acid, before any perceptible difference of temperature could obtain between the respective tubes (see Table A, columns 6 and 7).

Moreover, the exceptional negative position of the magnetised bar under the same temperature conditions, in the case of sulphuric acid, affords evidence that the effect was not due to these temperature causes. To more clearly demonstrate, however, that the results were mainly due to the influence of magnetisation, and acting on the kind suggestion of Professor G. G. Stokes, it was decided to make a duplex series of observations. I accordingly devised the modified form of apparatus fig. 2, which was intended to eliminate possible sources of error from temperature difference, by keeping the **U**-tube surrounded by a large volume of cold water during the experiments; the solution in the respective tubes being thus maintained under equal conditions. In comparing the results obtained with the two forms of apparatus, it should be borne in mind that, when using the apparatus fig. 2, the cold water surrounding the **U**-tube would have a tendency to retard the increase of the temperature of the solutions naturally arising from chemical combination. Further, the coil in fig. 2 being at one end of the long bar would be calculated to modify the magnetisation of the other end of the metal in the solution, compared with its action in fig. 1, where the coil almost entirely surrounded the bar: hence in fig. 2, the coil was made somewhat larger to overcome this to some extent, and the end of the bar B was shortened in experiments with fig. 2, so that this bar would be less liable to be affected magnetically by the external influence of the larger coil. I hope that the confirmatory results obtained in the two sets of observations may be considered as fairly satisfactory.

Table A.

Time from commencement and duration of magnetisation in minutes.		E.M.F. in volt, and electrochemical position of magnetised bar compared with the unmagnetised bar, the positive or negative position of the former being respectively indicated by the signs + and -.					
		Column 1.		Column 2.		Column 3.	
		Potassium chlorate and one-fifth nitric acid.		Potassium chlorate and one-third nitric acid.		Potassium chlorate and hydrochloric acid.	
		I.	II.	I.	II.	I.	II.
hrs.	mins.						
0	0	0·000	0·000	0·000	0·000	0·000	0·000
0	1	..	+0·004	+0·014	+0·002	..	..
0	2	..	..	..	+0·003	..	..
0	2½	..	+0·006	+0·014	+0·004	..	+0·002
0	3	..	..	..	+0·005	..	..
0	4	..	..	+0·016	+0·006	..	..
0	5	+0·005	+0·006	+0·011	+0·007	+0·002	+0·003
0	6	..	..	..	+0·007	..	..
0	7	..	..	..	..	..	..
0	7½	..	+0·004	+0·011	+0·008	..	+0·006
0	8	..	..	..	..	..	..
0	9	..	..	..	..	..	..
0	10	+0·006	+0·004	+0·011	+0·008	+0·004	+0·004
0	11	..	..	..	..	..	..
0	12	..	..	..	..	..	..
0	12½	..	..	..	..	..	..
0	13	..	..	..	..	..	..
0	14	..	..	..	..	..	..
0	15	+0·005	+0·003	+0·010	+0·007	+0·003	+0·004
0	17½	..	..	..	+0·007	..	..
0	20	+0·006	+0·003	+0·010	+0·007	+0·007	+0·004
0	25	+0·006	+0·003	+0·010	+0·007	+0·008	+0·004
0	30	+0·007	+0·002	+0·010	+0·009	+0·007	+0·005
0	35	+0·007	+0·003	+0·011	+0·006	+0·009	+0·004
0	40	+0·007	+0·003	+0·011	+0·006	+0·008	+0·006
0	45	+0·008	+0·003	+0·012	+0·005	+0·007	+0·005
0	50	+0·009	+0·002	+0·011	+0·005	+0·006	+0·005
0	55	+0·008	+0·003	+0·012	+0·005	+0·007	+0·006
1	0	+0·007	+0·003	+0·013	+0·005	+0·007	+0·005
1	5	..	+0·005	..	+0·004	..	+0·009
1	15	..	..	..	+0·005	..	+0·006
1	30	..	+0·007	..	+0·006	+0·009	..
1	45	..	+0·006	..	..	+0·009	..
2	0	..	+0·005	..	+0·005	+0·011	..

Column 1.—The potassium chlorate was a saturated solution of the salt, to which was added one-fifth of its volume of nitric acid of sp. gr. 1·388 at 60° F.

Column 2.—The potassium chlorate was a saturated solution of the salt, to which was added one-half of its volume of nitric acid of sp. gr. 1·388.

Column 3.—The potassium chlorate was a saturated solution, to which was added an equal volume of hydrochloric acid of sp. gr. 1·16.

Column 4.—The potassium bi-chromate was a saturated solution, to which was added one-half of its volume of nitric acid of sp. gr. 1·388.

Column 5.—The ferric chloride was a saturated solution, to which was added one-half of its volume of nitric acid of sp. gr. 1·388.

Table A—*continued.*

Time from commencement and duration of magnetisation in minutes.		E.M.F. in volt, and electrochemical position of magnetised bar compared with the unmagnetised bar, the positive or negative position of the former being respectively indicated by the signs + and -.				
		Column 4.	Column 5.		Column 6.	
		Potassium bi-chromate and nitric acid.	Ferric chloride and nitric acid.		Nitric acid, sp. gr. 1·388, one part, and three parts water.	
		II.	I.	II.	I.	II.
hrs.	mins.					
0	0	0·000	0·000	0·000	0·000	0·000
0	1	..	..	-0·004	+0·026	+0·004
0	2	+0·009	..	+0·002	..	..
0	2½	+0·005	..	+0·002	+0·020	+0·005
0	3	+0·009	..	+0·011	+0·020	+0·007
0	4	+0·010	..	+0·013	+0·016	+0·009
0	5	+0·007	..	+0·013	+0·014	+0·009
0	6	..	..	+0·020	..	..
0	7	..	..	+0·016	..	..
0	7½	..	..	+0·006	+0·011	+0·011
0	8	..	..	+0·022	..	..
0	9	..	..	+0·034	..	+0·011
0	10	+0·006	..	+0·011	+0·008	+0·011
0	11	..	..	+0·014	..	..
0	12	..	..	+0·011	..	..
0	12½	+0·009	..	..	..	+0·010
0	13	..	..	+0·009	..	..
0	14	..	..	..	..	..
0	15	+0·004	..	+0·002	+0·009	+0·005
0	16	..	..	..	..	..
0	17	..	..	..	..	..
0	17½	..	..	+0·009	..	..
0	19	..	..	..	..	..
0	20	+0·007	+0·009	+0·007	+0·007	+0·005
0	22½	..	..	..	..	..
0	25	+0·005	+0·018	+0·004	+0·001	+0·003
0	30	+0·003	+0·038	+0·002	+0·001	+0·004
0	35	+0·001	+0·038	+0·003	+0·011	+0·004
0	40	+0·004	+0·023	+0·002	+0·012	+0·004
0	45	+0·001	+0·002	..	+0·013	+0·004
0	50	+0·002	+0·004	..	+0·009	+0·006
0	55	..	+0·005	..	+0·012	+0·007
1	0	+0·006	+0·006	+0·001	+0·013	+0·007
1	5	..	..	..	..	..
1	15	..	..	..	..	..
1	30	..	..	..	..	..
1	45	..	..	..	..	..
2	0	..	+0·007	..	..	..
2	20	..	..	..	..	..
3	0	..	..	..	..	..
3	15	..	..	..	..	..

Table A—*continued*.

Time from commencement and duration of magnetisation in minutes.		E.M.F. in volt, and electrochemical position of magnetised bar compared with the unmagnetised bar, the positive or negative position of the former being respectively indicated by the signs + and -.					
		Column 7.		Column 8.	Column 9.	Column 10.	
		Nitric Acid, sp. gr. 1·388, 1 part, and 4 parts water.		Aqua regia, 2 parts HNO <sub>3</sub> and 1 part HCl, diluted to one-half with water.	Hydrochloric acid, sp. gr. 1·16, diluted to one-half with water.	Sulphuric acid (concentrated), sp. gr. 1·84.	
		I.	II.	II.	II.	I.	II.
hrs.	mins.						
0	0	0·000	0·000	0·000	0·000	0·000	0·000
0	1	..	+0·004	+0·002	..	..	..
0	2½	..	+0·006	..	..	..	-0·001
0	3	..	+0·009	..	..	..	..
0	4	..	+0·012	..	..	..	..
0	5	+0·012	+0·011	+0·004	-0·0004	-0·003	-0·002
0	6	..	+0·010	..	..	..	..
0	7½	..	+0·007	+0·006	..	..	..
0	9	..	..	..	..	..	..
0	10	+0·011	+0·003	+0·011	-0·001	-0·004	-0·003
0	11	..	+0·005	..	..	..	..
0	12	..	+0·005	+0·013	..	..	..
0	12½	..	..	..	..	..	..
0	13	..	+0·005	..	..	..	..
0	14	..	+0·003	+0·014	..	..	..
0	15	+0·013	+0·001	+0·027	-0·001	-0·005	-0·005
0	16	..	..	+0·027	..	..	..
0	17	..	..	+0·014	..	..	..
0	19	..	..	..	..	..	..
0	20	+0·014	+0·004	+0·025	-0·001	-0·006	-0·005
0	22½	..	..	+0·010	-0·001	..	..
0	25	+0·013	+0·004	..	-0·001	-0·005	-0·006
0	30	+0·012	+0·005	+0·004	-0·001	-0·007	-0·006
0	35	+0·013	+0·005	..	-0·001	-0·008	-0·006
0	40	+0·012	+0·004	..	-0·001	-0·009	-0·006
0	45	+0·012	+0·003	+0·001	-0·001	-0·011	-0·005
0	50	+0·012	+0·003	..	-0·001	-0·012	-0·005
0	55	+0·012	+0·004	+0·001	-0·002	-0·014	-0·006
1	0	+0·011	+0·004	+0·001	-0·002	-0·016	-0·006
1	15	..	..	..	-0·003	-0·022	-0·007
1	30	..	..	..	-0·002	-0·022	-0·008
1	45	..	..	..	-0·004	..	-0·008
2	0	..	..	..	-0·004	..	-0·009
2	20	..	..	..	..	..	-0·028
3	0	..	..	..	..	..	-0·009
3	15	..	..	..	..	..	-0·021



The records in the above table under divisions I were experiments made with apparatus, fig. 1, the records entered under divisions II, relate to observations made with apparatus, fig. 2.

The records of the effects in the stronger solutions do not indicate the full extent of the electric action compared with that of the weaker solutions; because in the former case the tubes could only be partially filled, so as to prevent boiling over.

### *General Remarks.*

*Potassium Chlorate and Nitric Acid Solutions, Columns 1 and 2.*—At the termination of some of these experiments, the depth of colour of the solution surrounding the magnetised iron was perceptibly of a darker shade than the colour in the tube surrounding the unmagnetised bar, this was confirmed by Eggertz's carbon coloration test.

*Ferric Chloride and Nitric Acid, Column 5.*—At forty minutes from the commencement of one experiment in apparatus fig. 1, the record was an E.M.F. of 0.023 volt, the magnetised bar being positive; the battery was then attached to a smaller coil surrounding the other bar B, which was then magnetised instead of the bar A, and in course of five minutes a reduction in the positive position of bar A to an extent of 0.021 volt occurred. At forty-five minutes the battery was reconnected to the coil surrounding the bar A, producing a steady increase of positive position in that bar as recorded in Table A, column 5.

*Aqua Regia, undiluted.*—With this reagent in fig. 1 no very decided galvanic reaction took place until the bar had remained magnetised for some ten minutes, when violent effervescence occurred accompanied by evolution of dense reddish-brown fumes, the magnetised bar then becoming rapidly electropositive to an extent yielding an E.M.F. of about 0.110 volt. This position was subsequently more or less maintained for some ten minutes, the galvanometer, however, gradually falling to zero as the ebullition in both tubes subsided. This was a difficult experiment to make, owing to the very violent effervescence.

*Aqua Regia, diluted, Column 8.*—Up to the commencement of the effervescence no perceptible difference in the colour of the solution in the respective limbs of the U-tube was noticed; but immediately on the violent ebullition occurring, which took place generally about ten minutes from commencement, the solution surrounding the magnetised bar frequently became of a very much darker tint. This marked difference between the colour of the respective solutions in the two tubes was maintained for some time, afterwards the two solutions became apparently nearly chromatically equal. The electro-

chemical effect appeared to be less marked when using aqua regia containing excess of HCl. The relative electrochemical position of the two bars in such case being less divergent, the HCl appearing to act somewhat as a strong diluent.

*Hydrochloric Acid and Sulphuric Acid, Columns 9 and 10.*—Singular to say, the previously described magnetochemical effects were comparatively small when using such a powerful reagent as hydrochloric acid alone, either concentrated (sp. gr. 1.16) or diluted. When this acid was employed in conjunction with concentrated solution of potassium chlorate (Table A, column 3), the effects there recorded appeared due rather to the oxidising agency of the evolved chloric compounds; in the presence of magnetism, the reactions with this electrolyte were occasionally irregular, the excess of HCl appearing sometimes to interfere. Sulphuric acid, conc., also seemed to behave abnormally, though this acid does not ordinarily act strongly on iron. The experiments with both the above acids in course of a large number of observations, proved exceptions to the general rule. The magnetised bar in the sulphuric acid, conc., and also in the hydrochloric acid, diluted, became the electronegative metal, not only in the case of  $\text{H}_2\text{SO}_4$ , when using the apparatus fig. 1, but also when experimenting with the modified form, fig. 2. Occasionally, with sulphuric acid, conc., the magnetised bar was, on first magnetising it, slightly electropositive for a few minutes only; but afterwards became steadily negative.

Under the conditions of experimentation, the magnetised bars in the powerful oxidising reagents used almost invariably assumed the electropositive position, the presence of  $\text{H}\cdot\text{NO}_3$  appearing essential to the full development of the positive position of the bar under the influence of magnetism. On the contrary, the magnetised bar seemed to be the electronegative metal in  $\text{H}_2\text{SO}_4$ , conc., and also in the HCl (diluted), as electrolytes. The two latter reagents by their action on the metal generate gases of a reducing character. These exceptions are not, however, averse to the principle that magnetisation exerts an influence on the relative electrochemical position of a pair of iron bars, varying according to the nature of the solution and the extent to which one of them is magnetised. In the above exceptions, it is possible that the magnetised bar assumed the negative position consequent on its being the one more attacked, under magnetic influences, by the reagent; thus producing a greater evolution of reducing gases in the tube A containing the magnetised bar than in the other tube; this may perhaps explain the negative effect. The observations of this memoir therefore indicate that, under the powerful and rapidly oxidising conditions described, a magnetised bar becomes metal positive to an unmagnetised one, whereas in the exceptional instances above alluded to, the electronegative effect

occurs, possibly owing to the presence in the solution of such reducing agents as nascent hydrogen, &c.

In the present incomplete stage of the enquiry these remarks are only offered tentatively.

The effects could not be expected to be large; I anticipate, however, generally more marked results in a more powerful magnetic field, exerting its influence, perhaps, for longer periods; but I think the experiments now submitted appear sufficient at least to afford an indication that, under the conditions recorded, magnetisation exerts on iron, in some solutions, an appreciable effect. The results already obtained in this direction are so far interesting as to encourage further research into the nature of this novel and subtle phenomenon.

XXVII. "Note on the Functions of the Sinuses of Valsalva and Auricular Appendices, with some Remarks on the Mechanism of the Heart and Pulse." By M. COLLIER. Communicated by VICTOR HORSLEY, F.R.S., Professor Superintendent of the Brown Institution. Received June 9, 1887.

(Abstract.)

The object of the paper is to disprove the present apparently accepted idea, that the sinuses of Valsalva are mere bulgings of the arterial walls, formed by a reflex current induced by the sudden closure of the semilunar valves.

The existence of a reflex current is shown to be impossible, and the theory of the sudden opening and closure of the semilunar valves is strongly opposed.

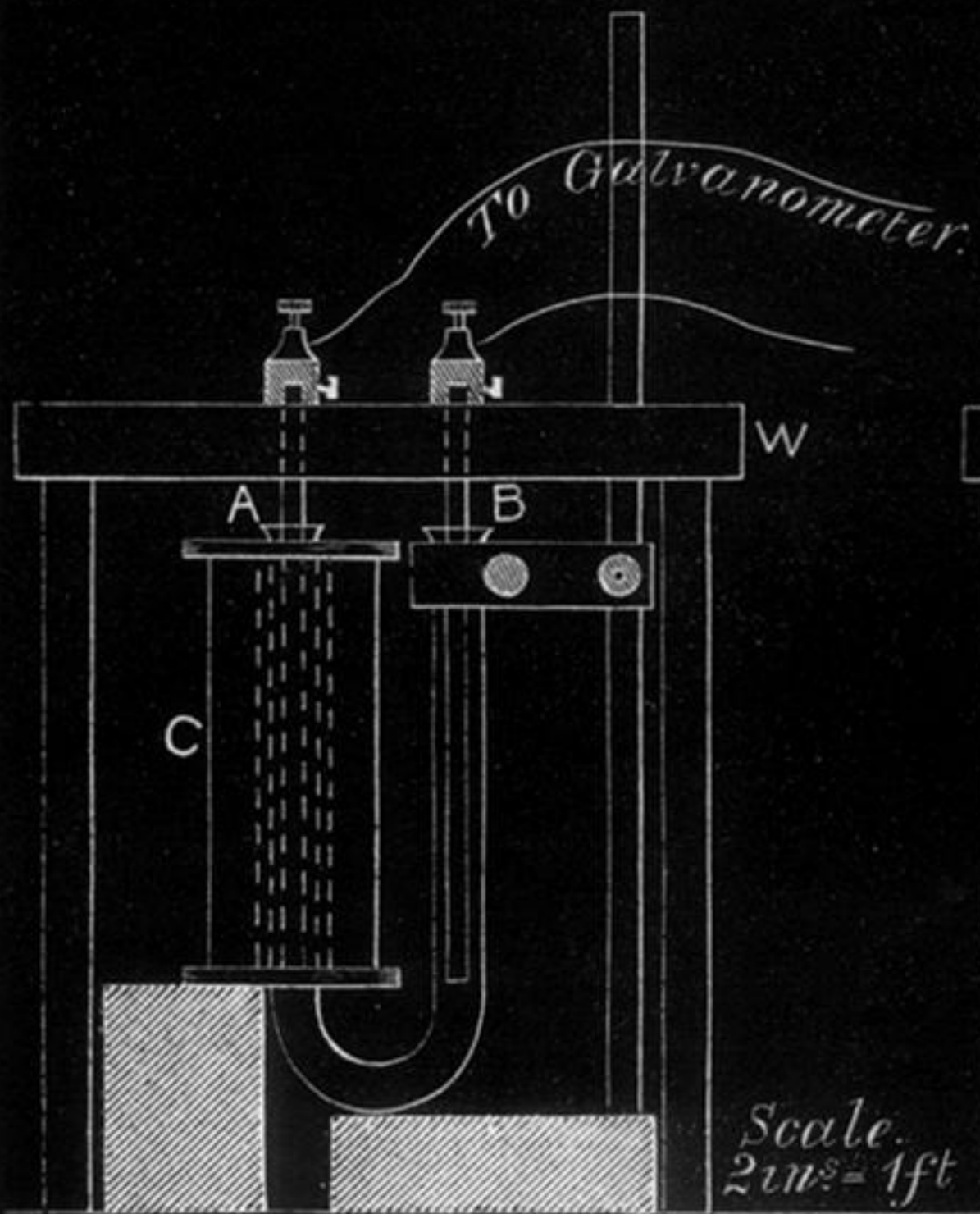
The presence of the sinuses of Valsalva is urged as an absolute essential to the mechanism of the heart's action. The paper then treats of the action of the auricle and the part played by the auricular appendix, the latter being considered as the only part of the auricle that sensibly and vigorously contracts.

The causes of the first sound of the heart are next alluded to, and the theory that the closure and vibration of the tricuspid and mitral valves assist in its production is refuted. The action of the ventricle and the mode of the injection of its contents into the aorta is dwelt upon at some length.

The latter part of the paper is devoted to the mechanism of the pulse, and an explanation is given of the so-called dicrotism.

The paper terminates with a summary of the chief points of the conclusions arrived at.

*Fig. 1*



*Fig. 2*

